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(54) Detergent compositions

Reinigungsmittel

Compositions détergentes

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Procter & Gamble Technical Centres Limited
Whitley Road
Longbenton
Newcastle upon Tyne, NE12 9TS (GB)

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(73) Proprietor: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

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(72) Inventors:
, Busch, Alfred
B-1820 Strombeek-Bever (BE)
, Baeck, Andre
B-2820 Bonheiden (BE)
, Dekker, Bob
B-1820 Strombeek-Bever (BE)

(74) Representative:
Peet, Jillian Wendy et al
Patent Department

Description

[0001] The present invention relates to detergent compositions containing a fabric - softening amount of a smectite-type clay. The clay is present in the form of agglomerates which comprise from 0.5% to 30% of an organic humectant.

5 [0002] British Patent 1,572,815 discloses a detergent composition based on soap and a curd-dispersing agent. The compositions comprise from 4% to 25% of a smectite-type clay. The clay is agglomerated with water, an aqueous electrolyte solution, a nonionic surfactant, or an aqueous solution of an organic adhesive. Examples of such adhesives include dextrin, gelatine, carboxymethyl-cellulose, starch, carboxymethyl starch, and alkyl and hydroxy alkyl substituted celluloses and starches. The agglomerates are disclosed to minimize dustiness while the full softening potential of the clay is preserved.

10 [0003] British Patent 1,167,037 discloses clays that have been treated with alkanolamine salts and an organic humectant. The treated clays are disclosed to hydrate rapidly and to develop viscosity in a short period of time as compared to untreated clays.

[0004] European Patent Application 164 797 discloses detergent compositions comprising agglomerates of smectite clay which are sprayed with a dispensing aid such as quaternary ammonium compounds.

15 [0005] French Patent Application 2 524 903 discloses detergent compositions comprising agglomerates of clay with binders such as sodium silicate, gums, resins and organic polymers.

[0006] European Patent Application 287344, published on 19th October, 1988, is a part of the prior art according to Article 54(3) EPC. It discloses softening clay in intimate contact with a nonionic surfactant system.

20 [0007] British Patent 1,400,898 discloses detergent compositions comprising, as a fabric softening ingredient, a smectite-type clay.

[0008] It is now well recognized in the detergent industry that clays of the type disclosed in British Patent 1,400,898 provide significant fabric softening benefits when used in a laundry detergent. Yet, it is equally well recognized that deposition of these clays onto the fabrics during the laundering process is far from complete; in fact, under typical European laundry conditions, less than half of the available clay is deposited onto the fabrics, the remainder being rinsed away with the laundry liquor during the subsequent rinsing steps. Moreover, the softening effect obtained as a result of the clay deposition is affected by factors that are not well understood.

[0009] It is, therefore, an object of the present invention to pretreat fabric - softening clays so as to increase the softening benefit obtained.

30 Summary of the Invention

[0010] The present invention relates to the granular detergent compositions comprising a) conventional detergent ingredients; and b) clay agglomerates comprising from 60% to 99.5% smectite-type clay and from 30% to 0.5% of an organic humectant. The humectants are selected from: glycerol, ethylene glycol, propylene glycol, dimers and trimers of glycerol and mixtures thereof. Highly preferred agglomerates further comprise, by weight of the clay, from 0.005% to 20% of a clay flocculating agent.

35 [0011] Preferred clay flocculating agents are polymers like poly(ethylene oxide), poly(acryl amide) and poly(acrylate), having a weight average molecular weight of from 100,000 to 10 million. Most preferred are poly(ethylene oxide) polymers having a molecular weight (weight average) in the range 150,000 to 5 million.

40 Detailed Description of the Invention

[0012] The detergent compositions of the present invention comprise conventional detergents, conventional detergent builders and, optionally, other conventional detergent ingredients. The compositions further comprise a fabric - softening amount, typically from 1% to 35% by weight preferably from 3% to 15% by weight of the detergent composition, of the fabric-softening clay agglomerates herein.

[0013] Percentages herein are percentages by weight of the detergent compositions, unless otherwise specified.

50 Detergent Ingredients

Detersive Surfactants -

[0014] The compositions of this invention will typically contain organic surface - active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such materials. Detersive surfactants useful herein include well - known synthetic anionic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkyl - and alkylether sulfates, paraffin sulfonates, olefin sulfonates, alkoxylated

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(especially ethoxylated) alcohols and alkyl phenols, amine oxides, alpha-sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. In general, such detergative surfactants contain an alkyl group in the C₉-C₁₈ range; the anionic detergative surfactants can be used in the form of their sodium, potassium or triethanolammonium salts; the nonionics generally contain from about 5 to about 17 ethylene oxide groups. U.S. Patent 3 995 669 contains detailed listings of such typical detergative surfactants.

[0015] $C_{11}\text{-}C_{16}$ alkyl benzene sulfonates, $C_{12}\text{-}C_{18}$ paraffin - sulfonates and alkyl sulfates, and the ethoxylated alcohols and alkyl phenols are especially preferred in the compositions of the present type. Also useful herein as the surfactant are the water- soluble soaps, e.g. the common sodium and potassium coconut or tallow soaps well - known in the art.

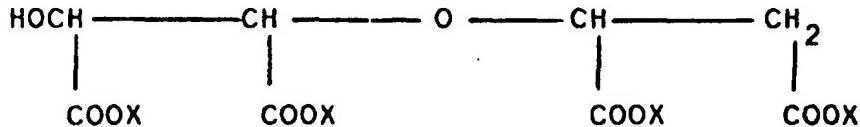
[0016] The surfactant component can comprise as little as 1% of the compositions herein, but preferably the compositions will contain 5% to 40%, preferably 10% to 30%, of surfactant. Mixtures of the ethoxylated nonionics with anionics such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabrics.

Detersive Adjuncts -

[0017] The composition herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that through-the-wash detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well - known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, carbonates, zeolites, water-soluble phosphates such as tri-polyphosphate and sodium ortho- and pyro - phosphates, silicates, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino - polyphosphonates (DEQUEST) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3 579 454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise about 0.5% to 45% of the composition. The 1-10 micron size zeolite (e. g. zeolite A) builders disclosed in German patent 2 422 655 are especially preferred for use in low - phosphate compositions.

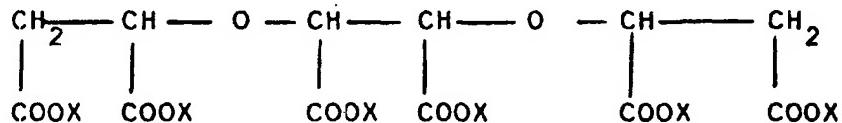
25 [0018] Particularly suitable phosphate-free builders are ether carboxylate mixtures comprising

a) from 1% to 99% of a tartrate monosuccinate component of the structure



wherein X is H or salt-forming cation; and

b) from 1% to 99% by weight of a tartrate disuccinate component of the structure:



wherein X is H or a salt-forming cation.

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[0019] Builder systems of this type are more fully disclosed in U.S. patent N° 4,663,071.

[0020] Typical detergent compositions contain from 5% to 35% of this builder system.

[0021] The laundry compositions herein also preferably contain enzymes to enhance their through - the - wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well - known in the art and in commercially available liquid and granular detergents. Commercial detergative enzymes (preferably a mixture of amylase and protease) are typically used at levels of 0.001% to 2%, and higher, in the present compositions. Detergent cellulase enzymes provide both cleaning and softening benefits, particularly to cotton fabrics. These enzymes are highly desirable in the detergent compositions of this invention.

[0022] The compositions herein can contain other ingredients which aid in their cleaning performance. For example, the compositions herein can advantageously contain a bleaching agent, especially a peroxyacid bleaching agent. In the context of the present invention, the term peroxyacid bleaching agent encompasses both peroxyacids per se and systems

which are able to yield peroxyacids *in situ*.

[0023] Peroxyacids *per se* are meant to include the alkaline and alkaline-earth metal salts thereof. Peroxyacids and diperoxyacids are commonly used; examples are diperoxydodecanoic acid (DPDA) or peroxyphthalic acid.

[0024] Systems capable of delivering peracids *in situ* consist of a peroxygen bleaching agent and an activator thereof.

[0025] The peroxygen bleaching agents are those capable of yielding hydrogen peroxide in an aqueous solution; these compounds are well - known in the art, and include hydrogen peroxide, alkali - metal peroxides, organic peroxide bleaching agents such as urea peroxide, inorganic persalt bleaching agents such as alkali metal perborates, percarbonates, perphosphates, persilicates, and the like.

[0026] Preferred are sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate and urea peroxyhydrate.

[0027] The liberated hydrogen peroxide reacts with a bleach activator to form the peroxyacid bleach. Classes of bleach activators include esters, imides, imidazoles, oximes, and carbonates. In these classes, preferred materials include methyl o-acetoxy benzoates; sodium-p-acetoxy benzene sulfonates such as sodium 4-nonanoxyloxybenzene sulfonate; sodium-4-octanoyloxybenzene sulfonate, and sodium-4-de-canoyloxybenzenesulfonate : biophenol A diacetate; tetra acetyl ethylene diamine; tetra acetyl hexamethylene diamine; tetra acetyl methylene diamine.

[0028] Other highly preferred peroxygen bleach activators which are disclosed in U.S. Patents 4,483,778 and 4,539,130 are alpha - substituted alkyl or alkenyl esters, such as sodium - 4(2 - chlorooctanoyloxy)benzene sulfonate, sodium 4-(3,5,5-trimethyl hexanoyloxy)benzene sulfonate. Suitable peroxyacids are also peroxygen bleach activators such as described in published European Patent Application N° 0 116 571, i.e., compounds of the general type RXAOOH and RXAL, wherein R is a hydroxcarbyl group, X is a heteroatom, A is a carbonyl bridging group and L is a leaving group, especially oxybenzenesulfonate.

[0029] Other highly desirable detergent ingredients for use in the detergent compositions of the present invention are quaternary ammonium compounds of the formula $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 8 to 20, preferably from 12-18 carbon atoms, R_5 is alkyl having from 1 to 10 carbon atoms, and R_6 and R_7 are each C_1 to C_4 alkyl preferably methyl : X^- is an anion, e.g. chloride. Examples of such quaternary ammonium compounds include $C_{12}-C_{14}$ alkyl trimethyl ammonium chloride and cocoalkyl trimethyl ammonium methosulfate. The quaternary ammonium compounds can be used at levels from 0.5% to 5%, preferably from 1% to 3%.

The fabric softening clay

[0030] Smectite-type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq/100g.

[0031] Montmorillonite clays are commonly used for this purpose. It appears, however, that certain hectorite clays provide better fabric softening performance than the more commonly used montmorillonites. The hectorites exhibiting this superior fabric softening performance are hectorites of natural origin having a lath - type shape.

[0032] According to the present invention, the fabric softening clay is present in the form of agglomerates. These agglomerates comprise, in addition to the clay, an organic humectant. The agglomerates optionally further comprise a polymeric clay flocculating agent. Typically, the agglomerates comprise by weight of the agglomerate, from 60% to 99.5% of the clay; from 0.5% to 30% of the humectant; and from 0% to 10% of the clay flocculating agent. Preferably, the agglomerates further contain a heavy metal sequestering agent. Examples include heavy metal chelators, like EDTA and ethylenediamine tetramethylene phosphonic acid (EDTP). The agglomerates typically contain from 0.1% to 10% of the chelator.

The humectant

[0033] The humectants are selected from glycerol, ethylene glycol, propylene glycol and the dimers and trimers of glycerol and mixtures thereof.

[0034] The clay agglomerates comprise from 0.5% to 30%, preferably from 2% to 15%, of the humectant.

The optional clay flocculating agent

[0035] Clay-flocculating agents are not commonly used in detergent compositions. On the contrary, one is inclined to use clay dispersants, which aid in removing clay stains from fabrics. Flocculating agents are, however, very well known in other industries like oil well drilling, and for ore flotation in metallurgy. Most of these materials are fairly long chain polymers and copolymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine. Gums, like guar gum, are suitable as well.

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[0036] Preferred are polymers of ethylene oxide, acryl amide, or acrylic acid. It has been found that these polymers dramatically enhance the deposition of a fabric softening clay if their molecular weights (weight average) are in the range of from 100,000 to 10 million. Preferred are such polymers having a (weight average) molecular weight of from 150,000 to 5 million.

[0037] The most preferred polymer is poly (ethylene oxide). Molecular weight distributions can be readily determined using gel permeation chromatography, against standards of poly (ethylene oxide) of narrow molecular weight distributions.

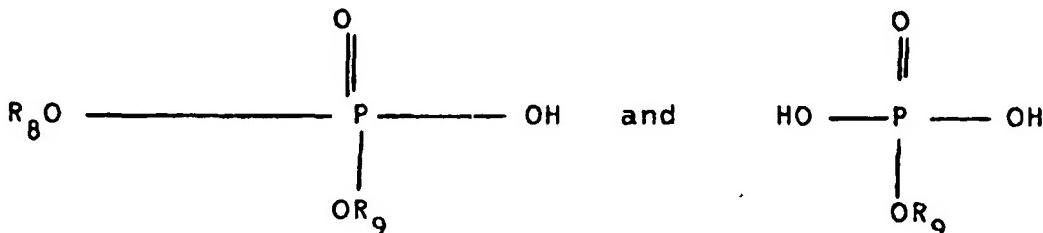
[0038] The clay agglomerates herein comprise, by weight of the clay, from 0% to 20% clay flocculating agent, preferably from 0.05% to 20% by weight of the clay if the molecular weight is 150,000 - 800,000 and from 0.005% to 2% by weight of the clay if its molecular weight is from 800,000 to 5 million.

10 Additional softening ingredients

[0039] The detergent compositions of the present invention may further contain, in addition to the clay material, other softening ingredients. Suitable examples include amines of the formula $R_1R_2R_3N$, wherein R_1 is C₆ to C₂₀ hydrocarbyl, R_2 is C₁ to C₂₀ hydrocarbyl, and R_3 is C₁ to C₁₀ hydrocarbyl or hydrogen. A preferred amine of this type is ditallowmethylamine.

[0040] Preferably, the softening amine is present: as a complex with a fatty acid of the formula RCOOH, wherein R is a C₉ to C₂₀ alkyl or alkenyl. It is desirable that the amine/fatty acid complex be present in the form of microfine particles, having a particle size in the range of from, e.g., 0.1 to 20 micrometers. These amine/fatty acid complexes are disclosed more fully in European Patent Application N° 0 133 804. Preferred are compositions that contain from 1% to 10% of the amine.

[0041] Suitable are also complexes of the above described amine and phosphate esters of the formula



wherein R_8 and R_9 are C₁ - C₂₀ alkyl, or ethoxylated alkyl groups of the general formula alkyl - (OCH₂CH₂)_y, wherein the alkyl substituent is C₁-C₂₀, preferably C₆-C₁₆, and y is an integer of 1 to 15, preferably 2-10, most preferably 2-5. Amine/phosphate ester complexes of this type are more fully disclosed in European Patent Application N° 0 168 889.

[0042] Further examples of optional softening ingredients include the softening amides of the formula $R_{10}R_{11}NCOR_{12}$, wherein R_{10} and R_{11} are independently selected from C₁-C₂₂ alkyl, alkenyl, hydroxy alkyl, aryl, and alkyl-aryl groups; R_{12} is hydrogen, or a C₁-C₂₂ alkyl or alkenyl, an aryl or alkyl-aryl group. Preferred examples of these amides are ditallow acetamide and ditallow benzamide. Good results are obtained when the amides are present in the composition in the form of a composite with a fatty acid or with a phosphate ester, as described hereinbefore for the softening amines.

[0043] The amides are present in the composition at 1% - 10% by weight.

[0044] Suitable softening ingredients are also the amines disclosed in U.K. Patent Application GB 2 173 827, in particular the substituted cyclic amines disclosed therein. Suitable are imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline wherein higher alkyl is alkyl having from 12 to 22 carbon atoms, and lower alkyl is alkyl having from 1 to 4 carbon atoms.

[0045] A preferred cyclic amine is 1-tallowamidoethyl-2-tallowimidazoline. Preferred compositions contain from 1% to 10% of the substituted cyclic amine.

[0046] The amine and amide softening ingredients may be added as a dry powder to a detergent granule, or may be sprayed onto the detergent granule or onto a carrier, either in melted or in dissolved form. An example of a suitable carrier is perborate monohydrate.

[0047] Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, bleach, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach activators and the like.

[0048] In a through - the - wash mode, the compositions are typically used at a concentration of at least 400 ppm,

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preferably 0.05% to 1.5%, in an aqueous laundry bath at pH 7-11 to launder fabrics. The laundering can be carried out over the range from 5°C to the boil, with excellent results.

Industrial Application

5 [0049] The agglomeration process itself may be performed using any of the techniques and apparatus which are conventional in the art (see e.g. "A review of Detergent Agglomeration" - M.J. DOLAN, HAPPI, April 1987 p 64-85). It can be batchwise or continuous. The optimum operating conditions (preferred granule size and moisture level) can be found by trial adjustments of process parameters such as the liquid spray - on level, rate and droplet size, the residence time, etc.

10 **EXAMPLE 1**

[0050] 40 kg of a commercial smectite clay (CEC . 50 meq/100g.) were sprayed with 5 l. of a 40% by weight aqueous solution of glycerol in a Lödige drum agglomerator. After drying and sieving, the following agglomerate composition was obtained :

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Smectite clay (anh.)	81.9%
Glycerol	4.1%
Moisture	14.0%

20

[0051] Granulometry : 212 µm (65 mesh) < min. 80% < 850 µm (20 mesh).

25 [0052] A reference agglomerate, i.e. no glycerol was made in the same way.

[0053] Both agglomerates were dry mixed with a spray-dried granular detergent to yield the following compositions:

	A	B
LAS	7	7
STPP	24	24
EDTA	0.2	0.2
Brightener	0.2	0.2
Sodium silicate	6.0	6.0
Suds suppressor	0.4	0.4
NA ₂ CO ₃	10.0	10.0
PB ₄ (*)	20.0	20.0
Proteolytic enzyme (*)	0.5	0.5
Na ₂ SO ₄ + H ₂ O	balance	
	93.5	93.5
Clay/ glycerol agglomerates	6.5	--
Clay Reference agglomerate	--	6.5
	100.0	100.0

(*) Dry mixed

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[0054] The compositions A and B were then used to wash 4 Kg clean fabric loads in a MIELE washing machine. The water hardness was 3.0 mmol (Ca⁺⁺ + Mg⁺⁺)/l and the detergent concentration was 10 g/l. Clean terry towel tracers were added to permit evaluation of 1 cycle and cumulative (4 cycles) softening performance. Softness tracers were line dried prior to assessment by expert judges. A 0 → 4 panel score units (p.s.u.) scale was used for grading, in which 0 means no difference and 4 stands for a very big difference.

[0055] Composition A was rated better for softness than B :

1 cycle tracers	0.6 p.s.u. (s)
4 cycle tracers	0.8 p.s.u. (s)
(s) Differences are statistically significant at 95% confidence level.	

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[0056] It can thus be seen that composition A, in accordance with the invention is superior in fabric softening performance to the prior art composition A.

[0057] The following agglomerate compositions are obtained, using the procedure outlined under Example I

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	II	III	IV	V
Smectite clay (anh.)	79.5%	83.4%	81%	74%
Ethylene glycol	8.0%	2.1%	-	6%
Sorbitol	-	-	4%	-
Polyethylene oxide (1)	-	-	-	5 %
Moisture	12.5%	14.5%	15%	13 %
EDTP	-	-	-	2 %

(1) having weight average molecular weight of about 300.000.

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[0058] The clay agglomerates may also be incorporated in a laundry additive, as such or with the aid of a water soluble and/or insoluble carrier such as e.g. a sheet or a pouch. These agglomerates, as such or with a suitable carrier, can then be added to the wash liquor on top of a conventional detergent composition. The laundry additive preferably also contains one or more of the additional softening ingredients specified before. The additive may thus be used in conjunction with detergent compositions that themselves do not contain such a clay and/or these other softening ingredients.

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Claims

1. A granular detergent composition comprising

a) conventional detergent ingredients; and

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b) clay agglomerates comprising from 60% to 99.5% by weight of smectite-type clay and

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characterised in that said clay agglomerates further comprise from 30% to 0.5% by weight of an organic humectant selected from:

glycerol, ethylene glycol, propylene glycol, dimers and trimers of glycerol, and mixtures thereof.

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2. A detergent composition of claim 1 wherein the clay agglomerates comprise from 2% to 15% by weight of the organic humectant.

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3. A detergent composition according to either of claims 1 or 2 characterised in that the clay agglomerates further comprise from 0.005% to 20% by weight of the day of a polymeric clay flocculating agent

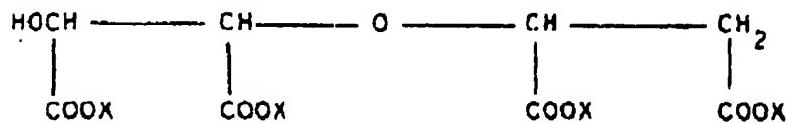
4. A detergent composition according to claim 3, characterised in that the clay agglomerates further comprise from 0.1% to 10% by weight of a chelator, preferably EDTA, EDTP, or mixtures thereof,

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5. A detergent composition according to Claim 3 wherein the polymeric clay flocculating agent has a weight average molecular weight of from 150.000 to 5 million.

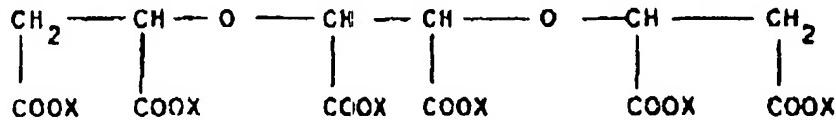
6. A detergent composition according to Claim 3 or 5 wherein the polymer is derived from monomers selected from ethylene oxide, acrylamide, and acrylic acid.
- 5 7. A detergent composition according to any one of the preceding claims, further comprising from 0.5% to 5% by weight of a quaternary ammonium compound of the formula $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 10 to 20 carbon atoms, R_5 , R_6 and R_7 are each C_1 to C_4 alkyl, and X^- is an anion.
- 10 8. A detergent composition according to any one of the preceding claims further comprising from 1% to 10% of an amide of the formula $R_{10}R_{11}NCOR_{12}$, wherein R_{10} and R_{11} are independently selected from C_1 - C_{22} alkyl, alkenyl, hydroxy alkyl, aryl, and alkyl-aryl groups; R_{12} is hydrogen, or a C_1 - C_{22} alkyl or alkenyl, aryl or alkyl-aryl group, or is $O-R_{13}$, wherein R_{13} is a C_1 - C_{22} alkyl or alkenyl, an aryl or alkyl-aryl group.
- 15 9. A detergent composition according to any one of the preceding claims further comprising from 1% to 10% by weight of imidazolines of the formula 1 - (R_{14}) amido (R_{15})-2-(R_{16}) imidazoline where R_{14} , R_{16} are independently selected from C_{12} - C_{22} alkyl and R_{15} from C_1 - C_4 alkyl.
- 20 10. A detergent composition according to any one of the preceding claims comprising from 1% to 10% by weight of amines of the formula $R_1R_2R_3N$ wherein R_1 is C_6 to C_{20} hydrocarbyl, R_2 is C_1 to C_{20} hydrocarbyl; and R_3 is C_1 to C_{10} hydrocarbyl or hydrogen.
11. A detergent composition according to any one of the preceding claims, further comprising from 5% to 35% by weight of a builder system, said builder system comprising

a) from 1% to 99% by weight of a tartrate monosuccinate component of the structure :



30 wherein X is H or a salt-forming cation; and

b) from 1% to 99% by weight of a tartrate disuccinate component of the structure :



40 wherein X is H or a salt-forming cation.

12. Use as a laundry additive of a clay agglomerate comprising from 70% to 99.5% by weight smectite type clay and from 30% to 0.5% by weight of an organic humectant as defined in Claim 1.
- 45 13. Use accordance with Claim 12 wherein the organic humectant represents from 2% to 15% by weight.
14. Use in accordance with Claims 12 and 13 wherein the agglomerate further comprises from 0.005% to 20% by weight of the clay of a polymeric clay flocculating agent.
- 50 15. Use in accordance with claims 12-14 wherein the laundry additive in addition comprises an additional softening ingredient as defined in claims 8, 9 and 10 in an amount of from 2% to 50% by weight, preferably from 5% to 30% by weight.
16. Use in accordance with claims 12-15, wherein the laundry additive is deposited onto/contained within a suitable water-soluble or water-insoluble carrier.

Patentansprüche

1. Körnige Detergenszusammensetzung, umfassend

5 a) herkömmliche Detergensbestandteile und

b) Tonagglomerate, welche 60 Gew.-% bis 99,5 Gew.-% eines Tons vom Smectittyp umfassen, und

10 dadurch gekennzeichnet, daß die genannten Tonagglomerate ferner 30 Gew.-% bis 0,5 Gew.-% eines organischen Feuchthaltemittels enthalten, welches unter: Glycerin, Ethylenglykol, Propylenglykol, Dimeren und Trimeren von Glycerin und Gemischen hiervon ausgewählt ist.

15 2. Detergenszusammensetzung nach Anspruch 1, worin die Tonagglomerate 2 Gew.-% bis 15 Gew.-% des organischen Feuchthaltemittels umfassen.

20 3. Detergenszusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Tonagglomerate ferner 0,005% bis 20%, bezogen auf das Gewicht des Tones, von einem polymeren Tonflockungsmittel umfassen.

4. Detergenszusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß die Tonagglomerate ferner 0,1 Gew.-% bis 10 Gew.-% eines Chelatbildners, vorzugsweise EDTA, EDTP, oder von Gemischen hiervon umfassen.

25 5. Detergenszusammensetzung nach Anspruch 3, worin das polymere Tonflockungsmittel ein Gewichtsmittel-Molekulargewicht von 150.000 bis 5 Millionen besitzt.

6. Detergenszusammensetzung nach Anspruch 3 oder 5, worin sich das Polymer aus Monomeren herleitet, die unter Ethylenoxid, Acrylamid und Acrylsäure ausgewählt sind.

25 7. Detergenszusammensetzung nach einem der vorherstehenden Ansprüche, welche ferner 0,5 Gew.-% bis 5 Gew.-% einer quaternären Ammoniumverbindung der Formel $R_4R_5R_6R_7N^+X^-$ umfaßt, worin R_4 ein Alkyl mit 10 bis 20 Kohlenstoffatomen darstellt, R_5 , R_6 und R_7 jeweils C₁-C₄-Alkyl darstellen und X^- ein Anion bedeutet.

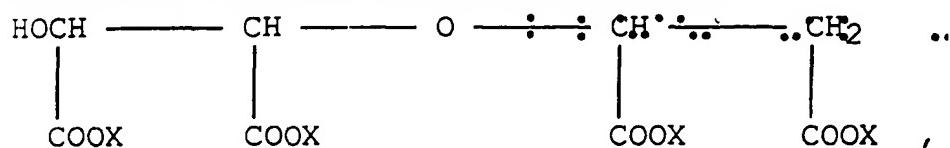
30 8. Detergenszusammensetzung nach einem der vorherstehenden Ansprüche, welche ferner 1% bis 10% eines Amids der Formel $R_{10}R_{11}NCOR_{12}$ umfaßt, worin R_{10} und R_{11} unabhängig voneinander unter C₁-C₂₂-Alkyl-, -Alkenyl-, -Hydroxyalkyl-, Aryl- und Alkyl-Arylgruppen ausgewählt sind; R_{12} für Wasserstoff oder eine C₁-C₂₂-Alkyl- oder -Alkenyl-, Aryl- oder Alkyl-Arylgruppe steht, oder O- R_{13} ist, worin R_{13} eine C₁-C₂₂-Alkyl- oder -Alkenyl-, eine Aryl- oder Alkyl-Arylgruppe bedeutet.

35 9. Detergenszusammensetzung nach einem der vorherstehenden Ansprüche, welche ferner 1 Gew.-% bis 10 Gew.-% von Imidazolinen der Formel 1-(R_{14})Amido(R_{15})-2-(R_{16})Imidazolin umfaßt, worin R_{14} , R_{16} unabhängig voneinander aus C₁-C₂₂-Alkyl ausgewählt sind und R_{15} aus C₁-C₄-Alkyl ausgewählt ist.

40 10. Detergenszusammensetzung nach einem der vorherstehenden Ansprüche, umfassend 1 Gew.-% bis 10 Gew.-% von Aminen der Formel $R_1R_2R_3N$, worin R_1 für eine C₆-C₂₀-Kohlenwasserstoffgruppe steht, R_2 eine C₁-C₂₀-Kohlenwasserstoffgruppe bedeutet, und R_3 eine C₁-C₁₀-Kohlenwassergruppe oder Wasserstoff darstellt.

45 11. Detergenszusammensetzung nach einem der vorherstehenden Ansprüche, welche ferner 5 Gew.-% bis 35 Gew.-% eines Gerüststoffsystems umfaßt, welches Gerüststoffsystem

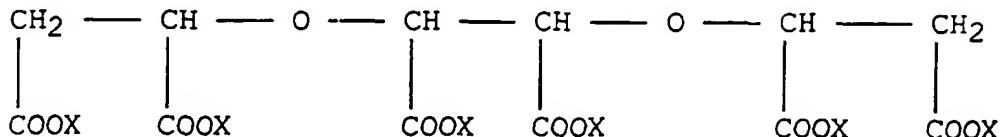
50 a) 1 Gew.-% bis 99 Gew.-% einer Tartratmonosuccinatkomponeute der Struktur:



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worin X für H oder ein salzbildendes Kation steht; und

b) 1 Gew.-% bis 99 Gew.-% einer Tartratdisuccinatkomponente der Struktur:



10 umfaßt, worin X für H oder ein salzbildendes Kation steht.

12. Verwendung eines Tonagglomerats als Wäschewaschzusatz, welches Tonagglomerat 70 Gew.-% bis 99,5 Gew.-% eines Tones vom Smectityp und 30 Gew.-% bis 0,5 Gew.-% eines organischen Feuchthaltemittels, wie es in Anspruch 1 definiert ist, umfaßt.
- 15 13. Verwendung nach Anspruch 12, wobei das organische Feuchthaltemittel 2 Gew.-% bis 15 Gew.-% darstellt.
14. Verwendung nach den Ansprüchen 12 und 13, wobei das Agglomerat ferner 0,005% bis 20%, bezogen auf das Gewicht des Tones, von einem polymeren Tonflockungsmittel umfaßt.
- 20 15. Verwendung nach den Ansprüchen 12 bis 14, wobei der Wäschewaschzusatz ferner einen zusätzlichen weichmachenden Bestandteil, wie er in den Ansprüchen 8, 9 und 10 definiert ist, in einer Menge von 2 Gew.-% bis 50 Gew.-%, vorzugsweise von 5 Gew.-% bis 30 Gew.-% umfaßt.
- 25 16. Verwendung nach den Ansprüchen 12 bis 15, wobei der Wäschewaschzusatz auf einem geeigneten wasserlöslichen oder wasserunlöslichen Träger abgelagert oder darin enthalten ist.

30 **Revendications**

1. Composition détergente granulée comprenant:

a) des ingrédients détergents classiques et

35 b) des agglomérats d'argile comprenant de 60% à 99,5% en poids d'argile de type smectite et

caractérisée en ce que lesdits agglomérats d'argile comprennent en outre de 30 à 0,5 % en poids d'un agent mouillant organique choisi parmi : le glycérol, l'éthylèneglycol, le propylèneglycol, les dimères et les trimères de glycérol, et leurs mélanges.

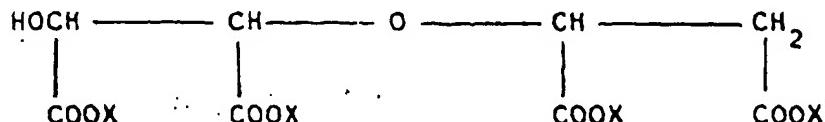
- 40 2. Composition détergente selon la revendication 1, dans laquelle les agglomérats d'argile comprennent de 2 à 15% en poids de l'agent mouillant organique.
3. Composition détergente selon l'une quelconque des revendications 1 ou 2, caractérisée en ce que les agglomérats d'argile comprennent en outre de 0,005% à 20% en poids de l'argile d'un agent de flocculation polymère d'argile.
- 45 4. Composition détergente selon la revendication 3, caractérisée en ce que les agglomérats d'argile comprennent en outre de 0,1% à 10% en poids d'un complexant, de préférence l'EDTA, l'EDTP, et leurs mélanges.
5. Composition détergente selon la revendication 3, dans laquelle l'agent de flocculation polymère de l'argile a une masse moléculaire moyenne en poids de 150 000 à 5 millions.
- 50 6. Composition détergente selon la revendication 3 ou 5, dans laquelle le polymère est dérivé de monomères choisis parmi l'oxyde d'éthylène, l'acrylamide, et l'acide acrylique.
7. Composition détergente selon l'une quelconque des revendications précédentes, comprenant en outre de 0,5% à 5% en poids d'un ammonium quaternaire de formule $R_4R_5R_6R_7N^+X^-$, dans laquelle R_4 représente un alkyle ayant de 10

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à 20 atomes de carbone, R₅, R₆ et R₇ représentent chacun un alkyle en C₁ à C₄, et X-représente un anion.

- 5 8. Composition détergente selon l'une quelconque des revendications précédentes, comprenant en outre de 1 à 10% d'un amide de formule R₁₀R₁₁NCOR₁₂, dans laquelle R₁₀ et R₁₁ sont choisis indépendamment parmi les groupes alkyl en C₁ à C₂₂, alcényle, hydroxy alkyle, aryle, et alkyl aryle; R₁₂ représente un atome d'hydrogène, ou un groupe alkyle ou alcényle en C₁ à C₂₂ ou un groupe aryle ou alkyl aryle, ou représente O-R₁₃, dans laquelle R₁₃ représente un groupe alkyle ou alcényle en C₁ à C₂₂, aryle ou alkyl aryle.
- 10 9. Composition détergente selon l'une quelconque des revendications précédentes, comprenant en outre de 1 à 10% en poids d'imidazolines de formule 1-(R₁₄)amido -(R₁₅)-2-(R₁₆)-imidazoline dans laquelle R₁₄, R₁₆, sont choisis indépendamment dans le groupe alkyle en C₁₂ à C₂₂ et R₁₅ parmi le groupe alkyle en C₁ à C₄.
- 15 10. Composition détergente selon l'une quelconque des revendications précédentes, comprenant de 1 à 10% en poids d'amines de formule R₁R₂R₃N dans laquelle R₁ représente un hydrocarbyle en C₆ à C₂₀, R₂ représente un hydrocarbyle de C₁ à C₂₀; et R₃ représente un hydrocarbyle en C₁ à C₁₀ ou un atome d'hydrogène.
11. Composition détergente selon l'une quelconque des revendications précédentes, comprenant en outre de 5 à 35% en poids d'un système d'adjuvants, ledit système d'adjuvants comprenant

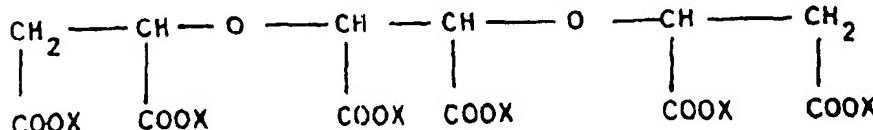
a) de 1% à 99% en poids d'un composant de tartrate monosuccinate de structure :



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dans laquelle X représente H ou un cation formant sel; et

b) de 1% à 99% en poids d'un composant tartrate disuccinate de structure:



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dans laquelle X représente H ou un cation formant sel.

- 40 12. Utilisation comme additif de lessive d'un agglomérat d'argile comprenant de 70% à 99,5% en poids d'argile de type smectite et de 30% à 0,5% en poids d'un agent mouillant organique tel que défini dans la revendication 1.
13. Utilisation selon la revendication 12, dans laquelle l'agent mouillant organique représente de 2 à 15 % en poids.
- 45 14. Utilisation selon les revendications 12 et 13, dans laquelle l'agglomérat comprend en outre de 0,005 % à 20 % en poids de l'argile d'un agent polymère de flocculation d'argile.
15. Utilisation selon les revendications 12 à 14, dans laquelle l'additif de lessive comprend en outre un ingrédient supplémentaire adoucissant tel que défini dans les revendications 8, 9 et 10 à raison de 2 % à 50 % en poids, de préférence de 5 à 30 % en poids.
- 50 16. Utilisation selon les revendications 12 à 15, dans laquelle l'additif de lessive est déposé sur/contenu dans un support approprié hydrosoluble ou insoluble dans l'eau.

